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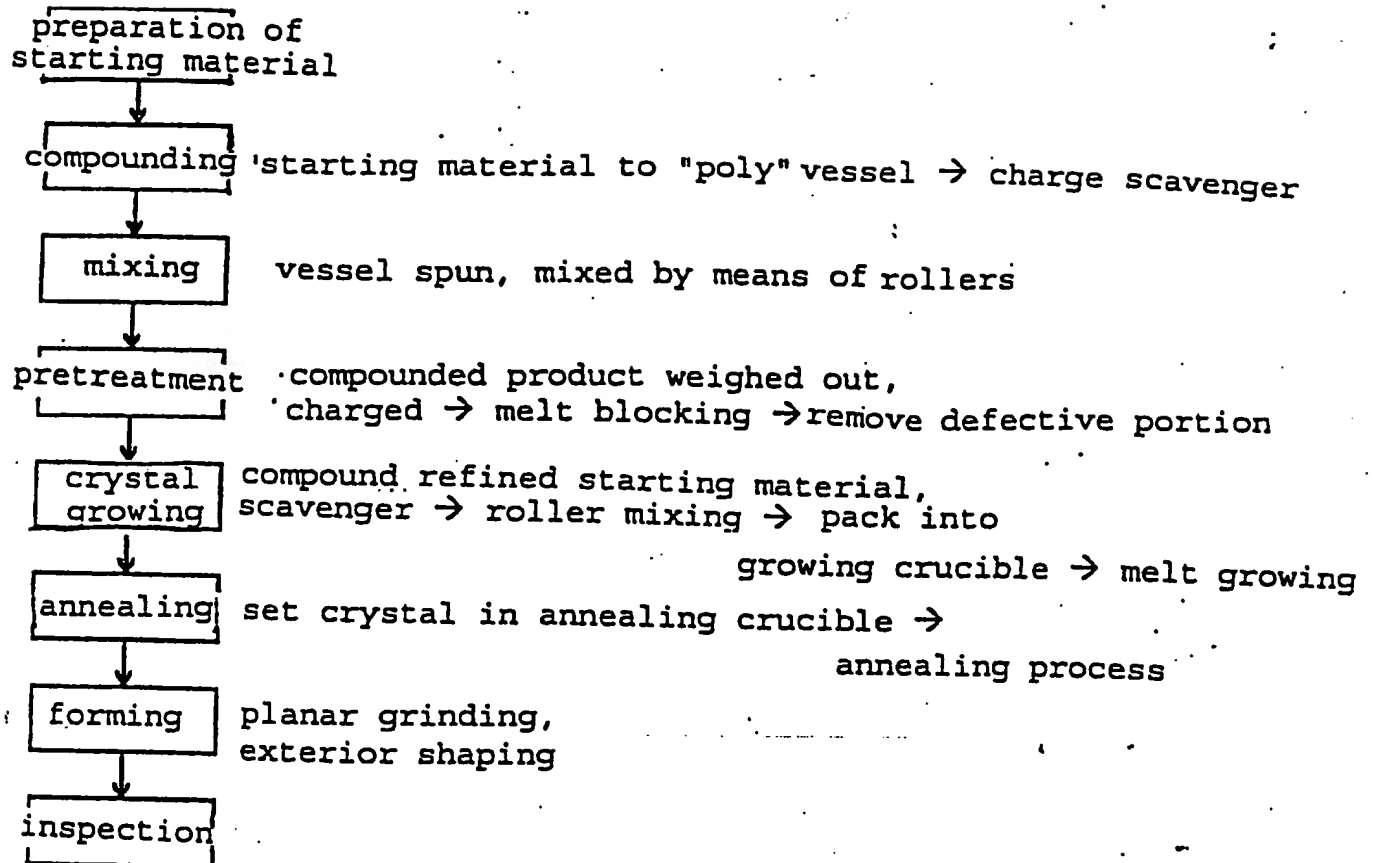
(54) [ Title of the Invention ] Production Method for  
Fluoride Crystal and Fluoride Crystal Lens

(57) [ Abstract ]

[ Problem ] To provide a fluoride that resists  
deterioration in transmissivity characteristics, even  
when irradiated repeatedly for extended periods with  
short wavelength, high energy light.

[ Solution ] The production method for fluoride crystal  
which pertains to the present invention is characterized  
by comprising a step in which a prepared fluoride  
starting material is mixed with a scavenger; a  
pretreatment step in which the mixed fluoride starting  
material is charged to a first crucible, melted, and then  
crystallized; a crystal growing step in which the  
pretreated fluoride starting material is charged to a  
second crucible larger than the first crucible, melted,  
and then gradually cooled; and an annealing step in which  
the grown fluoride crystal is heat treated; or  
alternatively comprising a step in which a prepared  
fluoride starting material is mixed with a scavenger; a  
pressing step in which the mixed fluoride starting  
material is pressed to produce a fluoride starting  
material aggregate; a crystal growing step in which the  
pressed fluoride starting material aggregate is charged  
to said crucible, melted, and then gradually cooled; and  
an annealing step in which the grown fluoride crystal is  
heat treated.

Fig. 1



[ Claims ]

[ Claim 1 ] Production method for fluoride crystal, characterized by comprising:

a step in which a prepared fluoride starting material is mixed with a scavenger;

a pretreatment step in which said mixed fluoride starting material is shaped into a disc;

a crystal growing step in which said mixed fluoride starting material that has been shaped into a disc in said pretreatment step is charged to a cylindrical crucible, melted, and then gradually cooled; and

an annealing step in which said grown fluoride is heat treated.

[ Claim 2 ] Production method for fluoride crystal, characterized by comprising:

a pretreatment step in which a prepared fluoride starting material is charged to a first crucible, melted, and then crystallized;

a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible having a diameter larger than the diameter of said first crucible, melted, and then gradually cooled; and

an annealing step in which said grown fluoride is heat treated.

[ Claim 3 ] Production method for fluoride crystal as set forth in Claim 1, characterized in that said fluoride starting material is passed through a mixing step for incorporating a scavenger.

[ Claim 4 ] Production method for fluoride crystal, characterized by comprising:

a step in which a prepared fluoride starting material is mixed with a scavenger;

a pretreatment step in which said mixed fluoride starting material is charged to a cylindrical first crucible, melted, and then crystallized;

a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible, melted, and then gradually cooled; and  
an annealing step in which said grown fluoride is heat treated.

[ Claim 5 ] Production method for fluoride crystal as set forth in Claim 4, characterized in that the diameter of said first crucible is equal to the diameter of the second crucible.

[ Claim 6 ] Production method for fluoride crystal as set forth in Claim 4, characterized in that the diameter of said first crucible is smaller than the diameter of the second crucible.

[ Claim 7 ] A production method for fluoride crystal, characterized by comprising:

- a step in which a prepared fluoride starting material is mixed with a scavenger;

- a pretreatment step in which said mixed fluoride starting material is charged to a cylindrical first crucible, melted, and then crystallized;

- a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible having a diameter greater than the diameter of said first crucible, melted, and then gradually cooled; and

- an annealing step in which said grown fluoride is heat treated.

[ Claim 8 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said fluoride is calcium fluoride.

[ Claim 9 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said fluoride is at least one member selected from magnesium fluoride, barium fluoride, neodymium fluoride, lithium fluoride, and lanthanum fluoride.

[ Claim 10 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized

in that said scavenger is zinc fluoride or bismuth fluoride.

[ Claim 11 ] Production method for fluoride crystal as set forth in any of Claims 1, 3, 4, and 7, characterized in that said mixing step includes a step of charging said fluoride and said scavenger to a vessel, and spinning said vessel to effect mixing.

[ Claim 12 ] Production method for fluoride crystal as set forth in Claim 1, characterized in that said pretreatment step includes a step of subjecting said mixed fluoride starting material to a melting process and shaping it into a disc.

[ Claim 13 ] Production method for fluoride crystal as set forth in Claim 1, characterized in that said pretreatment step includes a step of subjecting said mixed fluoride starting material to a pressing process and shaping it into a disc.

[ Claim 14 ] Production method for fluoride crystal as set forth in Claim 13, characterized in that said pressing process is a process characterized in that said mixed fluoride starting material is placed in a mould and placed under pressure of  $500 \text{ kg/cm}^2$  or above.

[ Claim 15 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said pretreatment step includes a step of removing the surface layer of the crystallized fluoride.

[ Claim 16 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said pretreatment step is followed by said crystal growing step, without grinding.

[ Claim 17 ] Production method for fluoride crystal as set forth in Claim 1, characterized in that the diameter of said cylindrical crucible is equal to the diameter of said mixed fluoride starting material once shaped into a disc in said pretreatment step.

[ Claim 18 ] Production method for fluoride crystal as set forth in Claim 1, characterized in that the diameter of said cylindrical crucible is greater than the diameter

of said mixed fluoride starting material once shaped into a disc in said pretreatment step.

[ Claim 19 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said crucible is a block type crucible.

[ Claim 20 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said crucible is a disc type crucible.

[ Claim 21 ] Production method for fluoride crystal as set forth in any of Claims 1, 2, 4, and 7, characterized in that said annealing process is followed by an external shaping process.

[ Claim 22 ] Production method for a fluoride crystal lens, characterized in that a lens is produced by external shaping processes of fluoride crystal obtained by the production method for fluoride crystal as set forth in any of Claims 1-21.

[ Claim 23 ] Production method for a fluoride crystal lens as set forth in any of Claims 1-21, further comprising the step of forming an antireflective film on said lens surface.

[ Claim 24 ] Production method for fluoride crystal, characterized by comprising:

- a step in which a prepared fluoride starting material is mixed with a scavenger;

- a pressing step in which said mixed fluoride starting material is pressed to produce a fluoride starting material aggregate;

- a crystal growing step in which said pressed fluoride starting material aggregate is charged to said crucible, melted, and then gradually cooled; and

- an annealing step in which said grown fluoride crystal is heat treated.

[ Detailed Description of the Invention ]

[ 0001 ]

[ Field of Industrial Utilization ] The present invention relates to fluoride crystal and to a production method for fluoride crystal, and more particularly to a

production method for fluoride crystal that can be used for a light-transmitting lens or other optical component in an excimer laser.

[ 0002 ]

[ Prior Art ] Excimer lasers have gained attention as the only lasers that can oscillate in the ultraviolet region, and have potential application in the electronics industry, chemical industry, and energy industry.

[ 0003 ] Specific applications include processing of metals, resins, glass, ceramics, semiconductors, and the like, chemical reactions, and so on.

[ 0004 ] Devices that can emit excimer laser light are known as excimer laser generator devices. A laser gas such as Ar, Kr, Xe, KrF, or ArF confined within a manifold is excited through irradiation with an electron beam, electrical discharge, or the like, whereupon excited atoms bond with ground state atoms to form molecules that exist only the excited state. These molecules are termed excimers. Since excimers are unstable, they rapidly emit ultraviolet light and drop back down to the ground state. This is termed bond-free transition; the ultraviolet light produced by the transition is amplified in an optical resonator comprising a pair of mirrors to produce laser light. [This is the principle of operation of] excimer laser generator devices.

[ 0005 ] Excimer laser light produced by KrF lasers and ArF lasers has wavelengths of 248 nm and 193 nm, respectively; light of this wavelength region is termed vacuum ultraviolet. The optical system used must have high transmissivity with respect to light in this wavelength region. Fluorides, typified by calcium fluoride, are favourable as glass materials for such optical systems.

[ 0006 ] Known fluorides include calcium fluoride, magnesium fluoride, barium fluoride, neodymium fluoride, lithium fluoride, and lanthanum fluoride.



[ 0007 ] A conventional production process for fluoride crystal will be described below using the example of calcium fluoride, also known as fluorite ( $\text{CaF}_2$ , expressed as a stoichiometric ratio).

[ 0008 ] Examples of conventional production processes for fluoride crystal are the methods taught in Unexamined Patent Application (Kokai) 4-349199 and Unexamined Patent Application (Kokai) 4-349198.

[ 0009 ] Briefly described, when a highly pure powder starting material prepared through chemical synthesis is subjected as-prepared to melting, there occurs an appreciable loss in weight due to factors pertaining to bulk specific gravity; for this reason, the high purity starting material is charged in cullet form to a crystal growing furnace.

[ 0010 ] Discoveries made by the inventors in the process of perfecting the present invention are described below. Fig. 8 is a flow chart of a fluoride crystal production process conducted by the inventors.

[ 0011 ] First, in Step S1, a powder starting material is prepared; in Step S2, this is charged to a vessel, melted, and then cooled. In Step S3, the hardened mass is ground in a stainless steel grinding machine. Subsequently, in Step S4, the ground mass is charged to a crystal growing crucible, melted, and then gradually cooled to grow a fluoride crystal. The purpose of Step S2 is to minimize change in bulk density before and after melting in Step S4.

[ 0012 ] The fluoride crystal produced in the foregoing manner is subjected to forming processes to produce a lens shape or the like for use as an optical component.

[ 0013 ] However, while fluoride crystals produced in the foregoing manner do exhibit satisfactory performance as components in ordinary visible light optical systems and exhibit properties superior to those produced using conventional methods, they nonetheless experience a deterioration in optical properties when repeatedly

irradiated for extended periods with high-energy, short-wavelength light, such as that from an excimer laser.

[ 0014 ] In the course of searching for the causes of this phenomenon, the inventors noted the effects of crystal structure and of contained impurities. They concluded that the problem is due to factors occurring in the fluoride crystal production process described earlier.

[ 0015 ] The inventors ascertained that in the production process described earlier, there occurs in step S3 introduction into the fluoride starting material of appreciable amounts of impurities such as water, iron (Fe), nickel (Ni), and chromium (Cr) from the outside. These impurities were ascertained to be responsible for the deterioration in properties occurring with repeated irradiation for extended periods with high-energy, short-wavelength light.

[ 0016 ] Further, in the process described earlier, a change in the bulk density of the fluoride occurs over Step S3 and Step S4, and thus the size of the resultant fluoride crystal is smaller than its size in the growing furnace. This represents a barrier to improving production efficiency and lowering manufacturing costs. Viewed another way, a large growing furnace must be provided where it is desired to produce a large fluoride crystal, and this will entail higher equipment costs.

[ 0017 ] Further, the melting step S2 and the grinding Step S3 lower the manufacturing time (throughput) [1].

[ 0018 ]

[ Problems Which the Invention Is Intended to Solve ] It is a principal object of the present invention to provide fluoride crystal that resists deterioration in transmissivity characteristics, even when irradiated repeatedly for extended periods with short wavelength, high energy light.

[ 0019 ] It is a further object of the invention to provide fluoride crystal suitable for use as an optical component in an excimer laser.

[ 0020 ] It is a still further object of the present invention to provide fluoride crystal that affords a highly reliable optical component.

[ 0021 ] It is a still further object of the present invention to provide fluoride crystal that can be produced at low cost by omitting the conventional grinding step.

[ 0022]

[ Means Used to Solve the Aforementioned Problems ] The production method for fluoride crystal, characterized by comprising a step in which a prepared fluoride starting material is mixed with a scavenger; a pretreatment step in which said mixed fluoride starting material is melted or pressed to shape it into a disc; a crystal growing step in which said mixed fluoride starting material that has been shaped into a disc in said pretreatment step is charged to a cylindrical crucible, melted, and then gradually cooled; and an annealing step in which said grown fluoride is heat treated.

[ 0023 ] [The invention] is further characterized in that said cylindrical crucible has a diameter equal to or greater than the diameter of said mixed fluoride starting material that is shaped into a disc in said heat treatment step.

[ 0024 ] [The invention] is further characterized by comprising a pretreatment step in which a prepared fluoride starting material is charged to a first crucible, melted, and then crystallized; a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible having a diameter larger than the diameter of said first crucible, melted, and then gradually cooled; and an annealing step in which said grown fluoride is heat treated.

[ 0025 ] [The invention] is further characterized by comprising a step in which a prepared fluoride starting material is mixed with a scavenger; a pretreatment step in which said mixed fluoride starting material is charged

to a cylindrical first crucible, melted, and then crystallized; a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible, melted, and then gradually cooled; and an annealing step in which said grown fluoride is heat treated.

[ 0026 ] Here, the diameter of the first crucible is equal to the diameter of the second crucible.

[ 0027 ] [The invention] is further characterized by comprising a step in which a prepared fluoride starting material is mixed with a scavenger; a pretreatment step in which said mixed fluoride starting material is charged to a cylindrical first crucible, melted, and then crystallized; a crystal growing step in which said pretreated fluoride starting material is charged to a cylindrical second crucible having a diameter greater than the diameter of said first crucible, melted, and then gradually cooled; and an annealing step in which said grown fluoride is heat treated.

[ 0028 ] The said pressing process is a process characterized in that said mixed fluoride starting material is placed in a mould and placed under pressure of 500 kgf/cm<sup>2</sup> or above. Said pretreatment step is characterized by removing the surface layer of the crystallized fluoride.

[ 0029 ] [The invention] is further characterized in that the pretreatment step is followed by said crystal growing step, without grinding. The crucible used is a crucible of block type or disc type.

[ 0030 ] In preferred practice, said scavenger is zinc fluoride. The fluoride of the present invention is characterized by consisting of calcium fluoride. [The invention] is further characterized in that the annealing process is followed by an external shaping process.

[ 0031 ] The production method for a fluoride crystal lens which pertains to the present invention is characterized in that a lens is produced by external shaping processes of fluoride crystal obtained by the

production method for fluoride crystal of the present invention.

[ 0032 ] [The invention] is characterized by further comprising the step of forming an antireflective film on said lens surface. "Content" (in ppm) as used herein, refers to the weight of the atom of interest (in  $\mu\text{g}$ ) per 1 g fluorite.

[ 0033 ]

[ Description of the Preferred Embodiments ] A first embodiment of the present invention will be described referring to Figs. 1-4. Fig. 1 is a flow chart depicting a production process for fluoride crystal pertaining to this first embodiment of the invention.

[ 0034 ] Fig. 2 depicts the refining furnace used for pretreatment. In Fig. 2, 201 denotes a refining furnace chamber, 202 denotes a heat insulating material, 203 denotes a heater, 204 denotes a first crucible, and 205 denotes a fluoride.

[ 0035 ] Fig. 3 depicts a block type growing furnace employed in the single crystal growing step. In the drawing, 301 denotes a growing furnace chamber, 302 denotes a heat insulating material, 303 denotes a heater, 304 denotes a second crucible, 305 denotes a fluoride, and 306 denotes a crucible lowering mechanism.

[ 0036 ] Fig. 4 depicts an annealing furnace employed in the annealing process. In the drawing, 401 denotes an annealing furnace chamber, 402 denotes a heat insulating material, 403 denotes a heater, 404 denotes a crucible, and 405 denotes a fluoride.

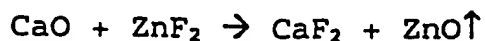
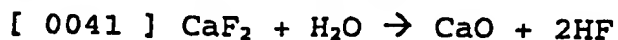
[ 0037 ] The following description of a preferred manufacturing process of the present invention takes the example of a calcium fluoride crystal as the fluoride.

[ 0038 ] (Preparation of Starting Material) The fluoride starting material can be fluorite mineral or a synthetic fluoride starting material. The latter is preferred for use in the present invention.

[ 0039 ] (Mixing Step) In this step, the calcium fluoride is mixed with a scavenger. The calcium fluoride

scavenger are placed in a vessel, and the vessel is used to effect mixing. Preferred scavengers are cadmium fluoride, lead fluoride, zinc fluoride, bismuth fluoride, calcium fluoride, lithium fluoride, and other compounds that bond with oxygen more readily than does the fluoride being grown. The selected material will react with oxides present in the synthetic fluoride starting material to form readily subliming oxides. Zinc fluoride or bismuth fluoride, which have especially low melting points, are preferred.

[ 0040 ] For example, a zinc fluoride scavenger will convert the calcium oxide formed in the presence of water into calcium fluoride.



The scavenger is added in proportions of at least 0.05 mol% and no more than 5.0 mol%, and preferably 0.1-1.0 mol%. The ZnO which forms will evaporate under the high temperature conditions in various processes.

[ 0042 ] (Pretreatment Step) Melting and crystallization of the fluoride starting material are carried out in a pretreatment step characterized in that the mixed fluoride starting material is placed in the first crucible 204, melted, and then crystallized. Melting is conducted at a temperature above the melting point of the fluoride, preferably 1390-1450°C. Crystallization is brought about through cooling of the molten fluoride.

Here, the resultant fluoride need not be a single crystal, and may be polycrystalline. The top layer (1-2 mm) of the resultant fluoride crystals is removed.

[ 0043 ] (Growing Step) In the single crystal growing step, the pretreated fluoride starting material is placed in a second crucible 304 that is larger than the first crucible 204. The crucible size ratio is 1 : 1.05-1 : 1.1 in order that the size (diameter) of the fluoride produced in the first crucible 204 is 0.9-0.95 x the size (diameter) of the second crucible 304. The crucible is heated to about 1390-1450°C to melt the fluoride, and the

crucible is then lowered at a rate of 0.1-5.0 mm/hr. While active cooling is not employed, the fluoride undergoes localized cooling as the crucible declines, resulting in crystallization. In the single crystal growing step, a scavenger is introduced into the growing furnace together with the fluoride starting material to eliminate calcium oxide.

[ 0044 ] (Annealing Step) Next, the grown fluoride 405 is heat treated. In the annealing process, the crucible 404 is heated to 900-1000°C by means of a heater 405. In preferred practice, the heating time is 20 hours or longer. Ideally, it is 20-30 hours.

[ 0045 ] According to the production method described above, there is virtually no change in bulk density before and after growing. Bulk density can be improved in the growing furnace. The resultant fluoride single crystal contains no more than 10 ppm impurities such as water, iron (Fe), nickel (Ni), and chromium (Cr).

[ 0046 ] The material is then subjected to forming processes to produce the desired optical component shape (convex lens, concave lens, disc, plate, etc.). Optionally, the fluoride crystal optical component may be provided on the surface thereof with an anti-reflective film. Anti-reflective films of magnesium fluoride, aluminum oxide, or tantalum oxide are preferred; these may be produced through deposition by resistance heating, ion beam deposition, sputtering, or the like. Optical components prepared in accordance with the present invention contain substantially no water, so bonding with the anti-reflective film is excellent.

[ 0047 ] Lenses produced in the foregoing manner may be assembled in various ways to construct an illumination optical system for a excimer laser, particularly an ArF excimer laser (optical system assembly step). An excimer laser light source, calcium fluoride lenses, and stage for transporting the substrate may then be assembled together to construct an exposing device.

[ 0048 ] This exposing device can be used to produce a latent image corresponding to a pattern to be formed by illuminating a photosensitive resist on a substrate with excimer laser light passed through a reticle pattern.

[ 0049 ] (Second Embodiment) In a second embodiment, starting material preparation and the mixing step are conducted analogously to the first embodiment, but the aforementioned pretreatment step is omitted, substituting a pressing step instead. Thus, the subsequent growing step also differs from the growing step in the first embodiment. However, the final annealing step is conducted analogously to the first embodiment.

[ 0050 ] The pressing step and growing step will now be described. Fig. 5 is a flow chart illustrating a fluoride crystal production process in accordance with the second embodiment of the present invention. Fig. 6 depicts pressing of the fluoride using a press machine for powder moulding.

[ 0051 ] (Pressing Step) The mixed fluoride 604 is placed in a mould 602 and subjected to pressing with a pressing member 603. This increases the bulk density. In preferred practice, the pressing force is 500 kgf/cm<sup>2</sup>.

[ 0052 ] (Growing Step) In the single crystal growing step, the pressed fluoride aggregate is placed in the second crucible 304 described earlier. The second crucible 304 is then heated to about 1390-1450°C by means of a heater 303 in order to melt the aggregate. The crucible lowering mechanism 306 is then used to lower the second crucible 304 at a rate of 0.1-5.0 mm/hr to bring about gradual cooling. The fluoride undergoes localized cooling as the second crucible 304 is lowered, resulting in crystallization.

[ 0053 ] (Third Embodiment) Fig. 7 is a simplified sectional view of an example of the growing furnace employed in a third embodiment for producing a fluoride crystal.



[ 0054 ] With this device, there is obtained a relatively thick fluorite crystal disc (disc-shaped fluorite crystal), so the device is termed a "disc type."

[ 0055 ] In Fig. 7, 701 denotes a growing furnace chamber, 702 denotes a heat insulating material, 703 denotes a heater, 704 denotes a small hole, 705 denotes a fluoride, 706 denotes a crucible lowering mechanism, 707 denotes a floor plate, and 708 denotes a cylindrical crucible. The cylindrical crucible 708 is partitioned into a plurality of spaces by the floor plates 707. The zones communicate through the small holes 704.

[ 0056 ] The third embodiment is analogous to the second embodiment apart from the growing furnace. In preferred practice, any one space in the disc type [furnace] is larger in diameter than the first crucible 205 of the first embodiment, the space being of a size such that a plurality of stacked fluorides 205 not subjected to a pretreatment process can be accommodated therein. Ideally, the space is of a size accommodating two stacked fluorides 205.

[ 0057 ] As regards fluoride aggregates produced by the pressing process in the second embodiment as well, any one space in a disc type [furnace] analogous to the first embodiment should be sufficient to accommodate a plurality of stacked fluorides starting material aggregates that have been subjected to this pressing process, and preferably to accommodate two stacked fluorides starting material aggregates that have been subjected to this pressing process.

[ 0058 ]

[ Examples ] [The invention] is now described in greater detail through Example 1. The procedure depicted in Fig. 1 was followed to produce calcium fluoride crystals. Each step is described below.

[ 0059 ] (Preparation of Starting Materials, Mixing Step) Calcium fluoride powder (fluoride starting material) was placed in a vessel, and a scavenger ( $\text{ZnF}_2$ ) was weighed out in an amount equivalent to 0.5 wt% of the starting

material and placed in the vessel. The size of the vessel was about twice the volume of the starting material. The vessel was spun for one hour to mix the starting material and the scavenger.

[ 0060 ] (Pretreatment Step) Pretreatment was conducted using the refining furnace depicted in Fig. 2.

[ 0061 ] The first crucible 204 was filled with the prepared starting material. The diameter of the first crucible 204 was 10% smaller than the diameter of the second crucible 304 used in the subsequent growing step.

[ 0062 ] The first crucible 204 was placed in the refining furnace and the chamber 201 of the refining furnace was evacuated to remove moisture from the fluoride 205.

[ 0063 ] The first crucible 204 was heated by means of the heater 203, conducting heating in such a way that the degree of vacuum was maintained at  $5 \times 10^{-4}$  torr until the melting temperature of the fluoride 205 was reached. The fluoride 205 melted at 1390-1450°C. All of the fluoride 205 packed into the first crucible 204 was melted.

[ 0064 ] Once melting temperature was reached, it was maintained until the degree of vacuum reached  $2 \times 10^{-6}$  torr.

[ 0065 ] Subsequently, power to heater 203 was turned off and cooled; upon cooling to room temperature, the crystallized fluoride starting material block 205 was removed from the refining furnace, and a 1 mm surface layer was removed therefrom.

[ 0066 ] (Growing Process) A calcium fluoride single crystal was grown using the growing furnace depicted in Fig. 3.

[ 0067 ] A  $\text{ZnF}_2$  scavenger was charged to the second crucible 304, and a stack of pretreated fluoride starting material blocks 205 was charged to the second crucible 304. The second crucible was then placed in the refining furnace. The amount of  $\text{ZnF}_2$  scavenger was equivalent to 0.2 wt% of the pretreated fluoride starting material.

[ 0068 ] The chamber 301 of the growing furnace was evacuated to remove moisture from the film 305.

[ 0069 ] The second crucible 304 was heated by means of the heater 303, conducting heating in such a way that the degree of vacuum was maintained at  $5 \times 10^{-4}$  torr until the melting temperature of the fluoride 305 was reached. The fluor[ide] 305 melted at 1390-1450°C. All of the starting material packed into the second crucible 304 was melted.

[ 0070 ] Once the melting temperature was reached, it was maintained until the degree of vacuum reached  $2 \times 10^{-6}$  torr. Once the temperature stabilized, it was held in this state for about 10 hours.

[ 0071 ] Next, the second crucible 304 was transported downwards by the lowering mechanism 306 at a rate of about 2 mm/h.

[ 0072 ] When the second crucible 304 reached the bottom, the voltage applied to the heater 303 was gradually reduced to produce a temperature drop off rate of about 100°C/h.

[ 0073 ] Subsequently, power to heater 303 was turned off, allowed to cool to room temperature, and the calcium fluoride single crystal was removed from the growing furnace.

[ 0074 ] (Annealing Step) The calcium fluoride single crystal was heat treated using the annealing furnace depicted in Fig. 4.

[ 0075 ] The calcium fluoride single crystal obtained through the growing step was placed in an annealing crucible 404. A  $\text{ZnF}_2$  scavenger, in an amount equivalent to 0.1 wt% based on the crystal, was scattered evenly in the gaps between the fluoride 405 and the crucible 404. The chamber 401 of the annealing furnace was evacuated and heated slowly by means of the heater 403. The temperature schedule is given below.

[ 0076 ] room temperature  $\rightarrow$  900°C (elevation rate +100°C/h)

held at 900°C (20 hr)

900°C  $\rightarrow$  room temperature (decline rate -6°C/hr)

Upon cooling to room temperature, the single crystal was removed from the furnace.

[ 0077 ] (Example 2) Preparation of starting materials and the mixing step in Example 2 were conducted analogously to Example 1, but the pretreatment process described above was omitted, substituting a pressing process. Thus, the subsequent process differed as well.

[ 0078 ] The growing step also differed from the growing step used in Example 1. However, the final annealing step was analogous to that used in Example 1. The pressing step and the growing step will now be described.

[ 0079 ] (Pressing Step) Pressing was conducted using the powder moulding press machine depicted in Fig. 6.

[ 0080 ] A suitable quantity of the prepared and mixed starting material powder was placed into a 128 [mm]φ mould 602 arranged on a stage 601 and pressed under pressure of about 700 kgf/cm<sup>2</sup> by means of a pressing member 603. Bulk density was increased by 1.5x.

[ 0081 ] (Growing Step) A calcium fluoride single crystal was grown using the growing furnace depicted in Fig. 3. The pressed starting material block was charged to a second crucible 304, and the second crucible 304 was placed in the growing furnace.

[ 0082 ] The chamber 301 of the growing furnace was evacuated to remove moisture from the fluoride 305.

[ 0083 ] The second crucible 304 was heated by means of the heater 303, conducting heating in such a way that the degree of vacuum was maintained at  $5 \times 10^{-4}$  torr until the melting temperature of the fluoride 305 was reached. The fluoride 305 melted at 1390-1450°C. All of the fluoride 305 packed into the second crucible 304 was melted.

[ 0084 ] Once the melting temperature was reached, it was maintained until the degree of vacuum reached  $2 \times 10^{-6}$  torr. Once the temperature stabilized, it was held in this state for about 10 hours.

[ 0085 ] Next, the second crucible 304 was transported downwards by the lowering mechanism 306 at a rate of about 2 mm/h.

[ 0086 ] When the second crucible 304 reached the bottom, the voltage applied to the heater 303 was gradually reduced to produce a temperature decline rate of about 100°C/h.

[ 0087 ] Subsequently, power to heater 303 was turned off, allowed to cool to room temperature, and the calcium fluoride single crystal was removed from the growing furnace.

[ 0088 ] The transmission spectra of the calcium fluoride single crystals prepared in Examples 1 and 2 were analysed; no absorption attributed to impurities was noted. The deterioration in transmissivity characteristics with exposure to an ArF laser was reduced, and optical characteristics were appreciably superior to those of calcium fluoride single crystals prepared by conventional methods.

[ 0089 ] In Example 1, virtually no change in bulk density before and after growing was noted, demonstrating that this method is preferable to that of Example 2. However, both Examples 1 and 2 gave crystals larger than those obtainable with conventional methods. In Example 2, the melting step and grinding step employed in conventional methods are replaced with a single pressing step, so throughput declines.

[ 0090 ] (Example 3) A calcium fluoride powder and  $\text{ZnF}_2$  scavenger were mixed analogously to Example 1.

[ 0091 ] Pretreatment was conducted using the refining furnace depicted in Fig. 2. The pretreatment method was analogous to that in Example 1. A point of difference is that the amount of starting material is less than in Example 1, with the size of the resultant fluoride being such that two stacked [fluorides] can be accommodated within each of the five growing chambers of the crucible 708 depicted in Fig. 7.

[ 0092 ] Next, a stack of two fluoride discs having been refined in the refining furnace was placed in each of the growing chambers of the crucible depicted in Fig. 7, a

scavenger was melted, and crystal growing was conducted under conditions analogous to Example 1.

[ 0093 ] Next, the grown fluoride crystal was placed in an annealing unit having a crucible of essentially the same construction as that shown in Fig. 7, and was subjected to heat treatment. The resultant calcium fluoride crystal was shaped to produce a lens.

[ 0094 ] The calcium fluoride lens exhibited good internal transmissivity, even when the lens was repeatedly irradiated for an extended period with excimer laser light from an exposing device used in semiconductor device manufacture.

[ 0095 ]

[ Effects of the Invention ] According to the present invention, contamination by impurities during the production process can be prevented, thereby affording a fluoride crystal with high transmissivity. Further, there is provided a highly reliable fluoride that resists deterioration in transmissivity characteristics, even when irradiated repeatedly for extended periods with short wavelength, high energy light.

[ 0096 ] According to the present invention, fluoride crystal optical components can be produced at low cost in a shorter production time.

[ Brief Description of the Figures ]

[ Figure 1 ] A flow chart illustrating a fluoride crystal production process according to a first embodiment of the present invention.

[ Figure 2 ] A simplified sectional view of an example of a refining furnace for producing fluoride crystal in accordance with the present invention.

[ Figure 3 ] A simplified sectional view of an example of a growing furnace for producing fluoride crystal in accordance with the present invention.

[ Figure 4 ] A simplified sectional view of an example of an annealing furnace for producing fluoride crystal in accordance with the present invention.

[ Figure 5 ] A flow chart illustrating a fluoride crystal production process according to a second embodiment of the present invention.

[ Figure 6 ] A simplified sectional view of an example of a pressing device for producing fluoride crystal in accordance with the present invention.

[ Figure 7 ] A simplified sectional view of an example of a refining furnace for producing fluoride crystal in accordance with the third embodiment of the present invention.

[ Figure 8 ] A simplified view of a fluoride crystal production process tested previously by the inventors.

[ Key ]

- 201: refining furnace chamber
- 202, 302, 402, 702: heat insulating material
- 203, 303, 403, 703: heater
- 204, 304, 404, 708: crucible
- 205, 305, 405, 705: fluoride
- 301: growing furnace chamber
- 306, 706: crucible lowering mechanism
- 401: annealing furnace chamber
- 604: fluoride
- 602: forming mould
- 603: pressing component
- 704: small hole
- 707: floor plate

preparation of  
starting material

↓  
compounding starting material to "poly" vessel → charge scavenger

↓  
mixing vessel spun, mixed by means of rollers

↓  
pretreatment compounded product weighed out,  
charged → melt blocking → remove defective portion

↓  
crystal growing compound refined starting material,  
scavenger → roller mixing → pack into

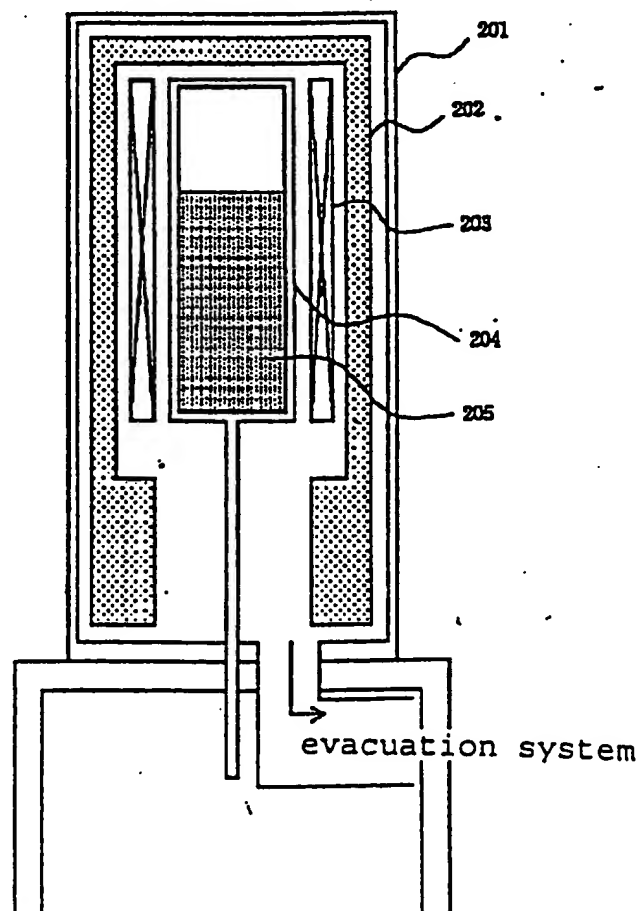
growing crucible → melt growing

↓  
annealing set crystal in annealing crucible →  
annealing process

↓  
forming planar grinding,  
exterior shaping

↓  
inspection

Fig. 2





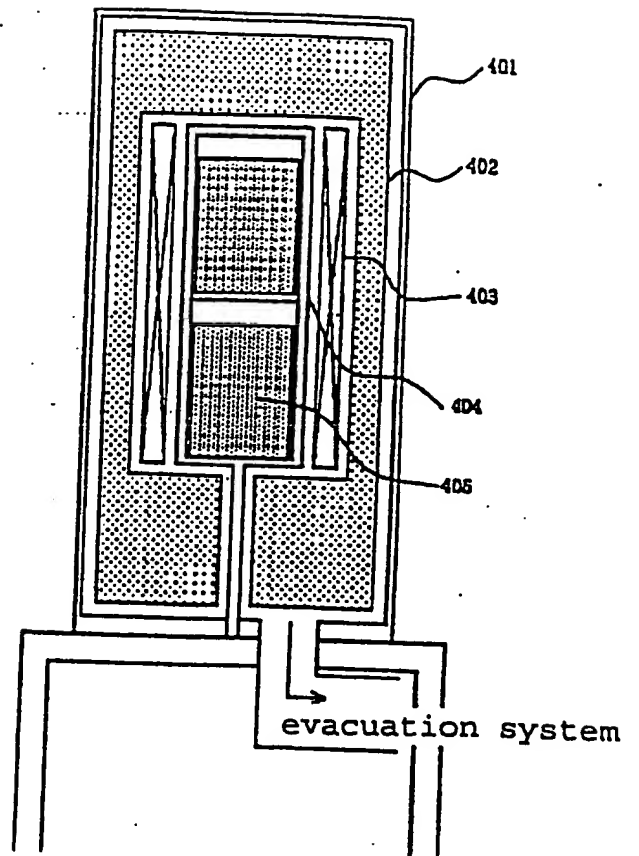
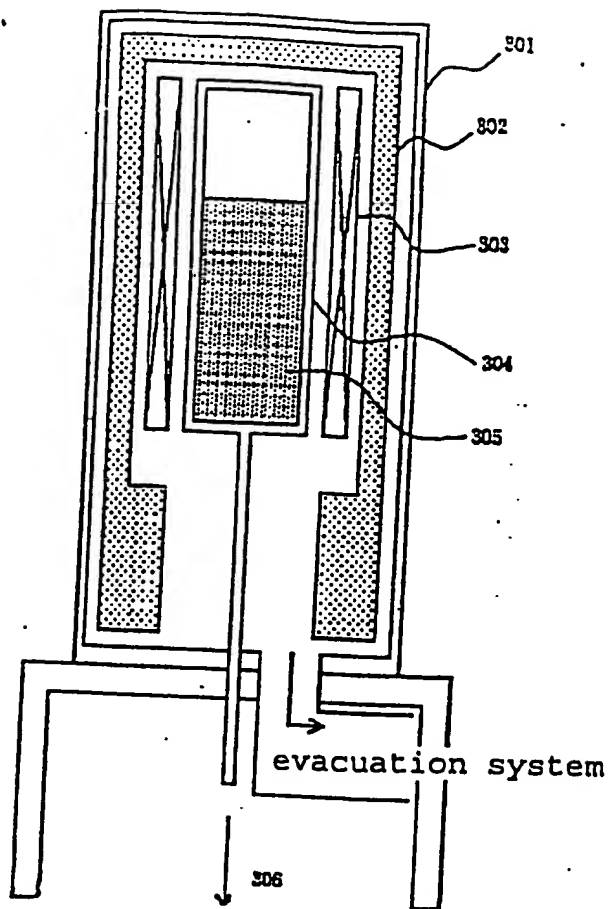
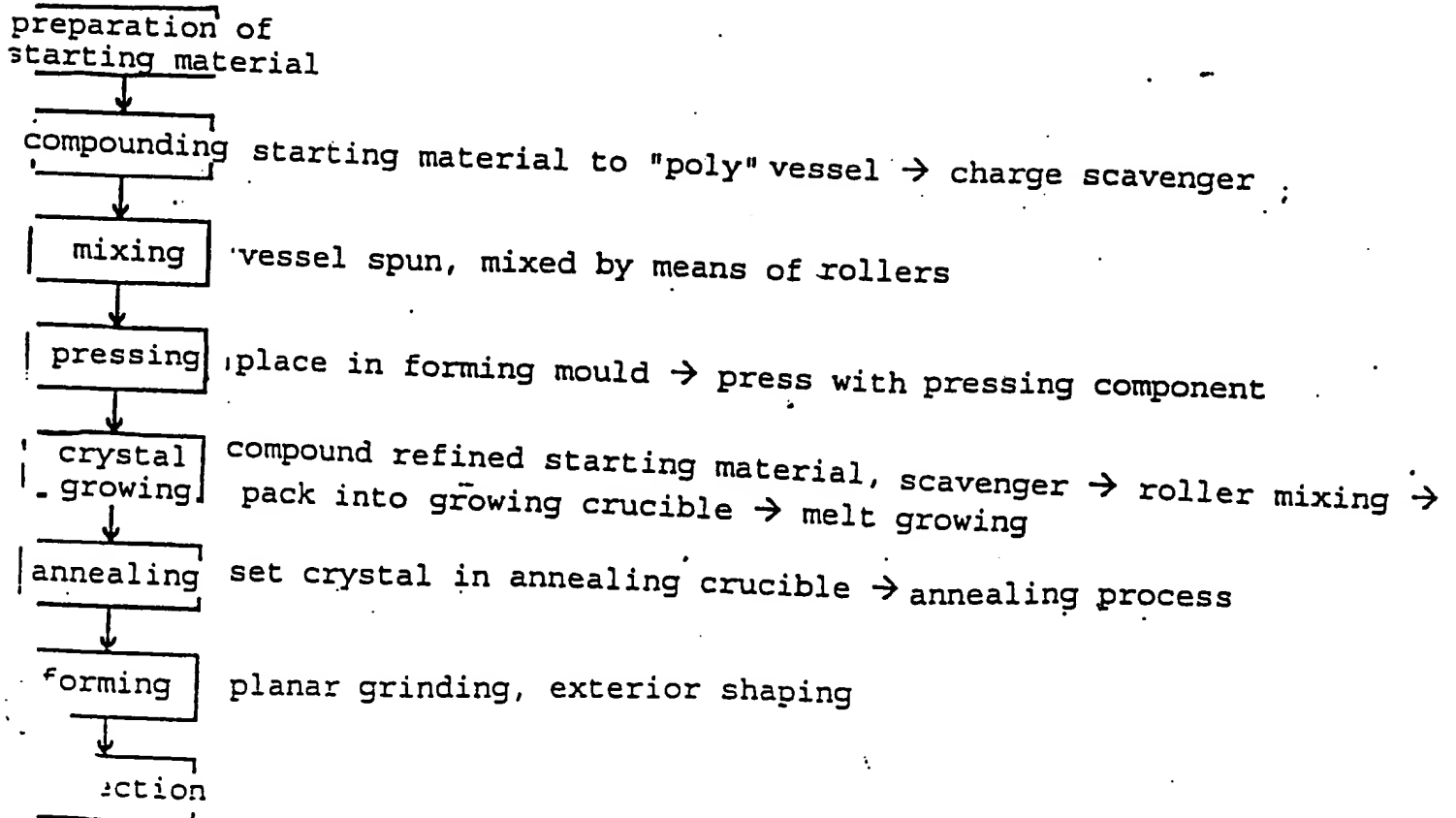


Fig. 5



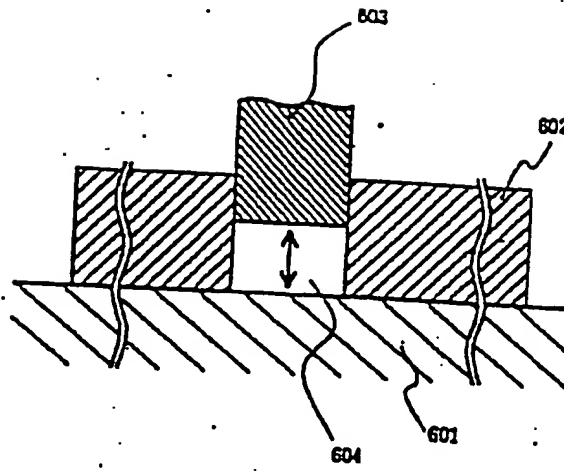


Fig. 7

Fig. 8

